

Physics of Quantum Structures in Photovoltaic Devices

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Abstract

There has been considerable activity recently regarding the possibilities of using various nanostructures and nanomaterials to improve photovoltaic conversion of solar energy. Recent theoretical results indicate that dramatic improvements in device efficiency may be attainable through the use of three-dimensional arrays of zero-dimensional conductors (i.e., quantum dots) in an ordinary p-i-n solar cell structure. Quantum dots and other nanostructured materials may also prove to have some benefits in terms of temperature coefficients and radiation degradation associated with space solar cells. Two-dimensional semiconductor superlattices have already demonstrated some advantages in this regard. It has also recently been demonstrated that semiconducting quantum dots can also be used to improve conversion efficiencies in polymeric thin film solar cells. Improvement in thin film cells utilizing conjugated polymers has also been achieved through the use of one-dimensional quantum structures such as carbon nanotubes. It is believed that carbon nanotubes may contribute to both the disassociation as well as the carrier transport in the conjugated polymers used in certain thin film photovoltaic cells. In this paper we will review the underlying physics governing some of the new photovoltaic nanostructures being pursued, as well as the current methods being employed to produce III-V, II-VI, and even chalcopyrite-based nanomaterials and nanostructures for solar cells.

Introduction

The underlying physics providing the impetus for the use of nanostructures in solar cells can be understood through elementary quantum mechanics. One of the first lessons learned in an introduction to the field is that electron motion is governed by Schroedinger's Equation and the potential $V(r)$

$$\frac{-\hbar^2}{2m} \nabla^2 \Psi(r) + V(r) \Psi(r) = E \Psi(r) \quad (1)$$

If $V(r) = 0$, the solution is a simple plane-wave. In regions where V is non-zero, and the electron has enough energy to pass over or tunnel through, we will have a modified plane-wave solution (scattering states). However, where $V(r)$ is negative we will have bound (negative energy) states. Although scattering and bound states differ in many ways, of particular interest is the fact that scattering states are continuous function of the electrons energy, whereas bound states are possible only for particular values of the energy. That is, bound states only occur for discrete values of energy (i.e., they are "quantized"). If two identical atoms are brought together, with an electron in the same quantum state, the energy levels must split due to the Pauli Exclusion Principle.

Solutions to Schroedinger's equation for electrons in a crystalline solid are called Bloch wavefunctions. Fourier's theorem shows that the functions are simply a plane-wave solution multiplied by a periodic function whose periodicity matches that of the potential in the crystal.

$$\Psi(r) = u(r) e^{ik \cdot r} \quad (2)$$

Confining Bloch electrons to a thin plane by providing a rectangular potential well perpendicular to the plane will also produce a discrete bound state spectrum. Such a system is an example of a Quantum Well (QW). If the electron is completely confined to the plane, due to an infinitely deep potential well of width a_z , the bound state energies are

$$E = \left(\frac{\hbar^2}{2m} \right) (k_x^2 + k_y^2) + \left(\frac{\hbar^2}{2m} \right) \left(\frac{\pi n_z}{a_z} \right)^2 \quad (3)$$

Similarly, if constrained in two dimensions we have a quantum wire with energy levels given by

$$E = \left(\frac{\hbar^2}{2m} \right) k_x^2 + \left(\frac{\hbar^2}{2m} \right) \left[\left(\frac{\pi n_y}{a_y} \right)^2 + \left(\frac{\pi n_z}{a_z} \right)^2 \right] \quad (4)$$

and if constrained in three dimension we have a quantum dot with energy levels given by

$$E = \left(\frac{\hbar^2}{2m} \right) \left[\left(\frac{\pi n_x}{a_x} \right)^2 + \left(\frac{\pi n_y}{a_y} \right)^2 + \left(\frac{\pi n_z}{a_z} \right)^2 \right] \quad (5)$$

In the same way that bringing a number of atoms together in a solid results in “energy bands,” bringing a number of quantum structures together (i.e., multiple quantum wells, ordered arrays of quantum wires or quantum dots) will also result in bands. If these collections of quantum structures reside within a host semiconductor we will have what are called “minibands” (see Figure 1) Electronic States in “wells” are “quantized” and therefore have discrete-like energy levels. The mini-band levels depend on the width of the wells. These size dependent mini-bands levels afford photovoltaic designers the flexibility to tune the absorption spectrum of devices beyond what is available through the normal array of bulk semiconductor bandgaps. In addition to adjusting the absorption spectrum of the device, these minibands also provide the possibility to take advantage of such things as two-photon processes and slow-cooling effects.

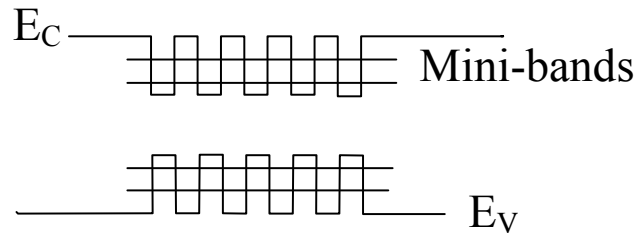


Figure 1. Idealized energy band diagram of a multiple quantum well structure showing electronic “mini-bands”.

To a first order approximation the effective bandgap of a semiconducting quantum dot can be calculated using

$$\hbar\omega = E_g + \frac{\hbar^2}{2m_e^* r^2} \pi^2 \quad (6)$$

Thus, for a real material the appropriate size to achieve mid-gap state in a suitable device structure can be determined. Figure 2. shows a atomic force microscopy image of InAs quantum dots grown by metal organic chemical vapor deposition on InGaAs at Essential Research Incorporated and imaged in the NanoPower Research labs at Rochester Institute of technology.

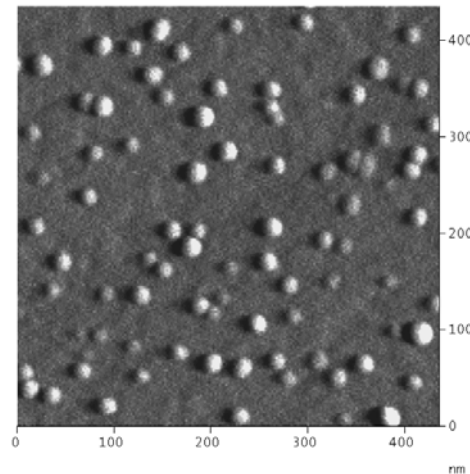


Figure 2. Atomic force micrograph of InAs quantum dots grown on InGaAs.

Historical Developments

An antecedent to the use of nanostructures for photovoltaics lies in what has been referred to as the "impurity photovoltaic effect (IPV)"[1]. M. Wolf suggested in 1960 that impurities could be added in such a way to a conventional *p-n* junction solar cell that they would create available electronic states within the bandgap (see Figure 3). These states could then participate in sub-bandgap absorption and act to raise the overall efficiency of a solar cell. However Shockley and Queisser, early modelers of single junction photovoltaic, argued against the IPV by cited that the recombination losses, which would result from the introduction of the impurities would make IPV devices impractical [2].

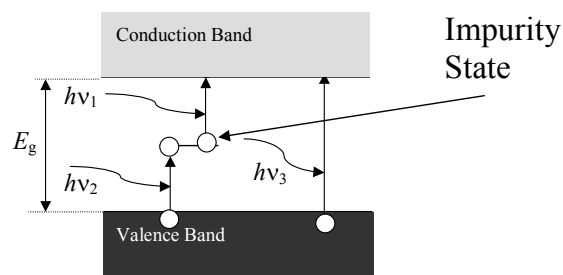


Figure 2. Idealized energy band diagram outlining the impurity photovoltaic effect.

Photovoltaics designers were able to finally overcome the single junction Shockley - Quiesser model limit through the use of tandem cells. Even multijunction solar cells have their theoretical limitations imposed by such things as current matching of the junctions and the actual materials issues imposed by non-idealized or real materials. Theoretically, at least, designers could envision solar cell efficiencies that dwarfed the single-junction limit by the use of an ever-increasing number of junctions.

In 1990, a new approach to the possible design of solar cells was put forth in a seminal paper by Barnham and Duggen (see Figure 4) [3]. They proposed that the limits imposed on a tandem cell could be eliminated through the use of multiple quantum wells (MQW). This work was followed by suggestions that the use of these and similar nanostructured approaches could yield other benefits such as inverse Auger mechanisms with quantum efficiencies greater than one [4-5]. Luque and Marti showed that a quantum dot array incorporated in a $p-i-n$ junction solar cell could dramatically exceed the Shockley - Quissier limit and even that of an ideal tandem cell (see Figure 5) [6]. The proposed use of quantum dots for spectral shifting and concentrator applications has also generated interest [7]. However, the largest impact in the development of photovoltaics from quantum dots has been their use as additives in thin film polymeric solar cell development [8]. It has been demonstrated that these quantized nanostructured materials will act as disassociation centers for the excitons created in the conjugated polymeric absorbers and can help facilitate carrier transport through these devices.

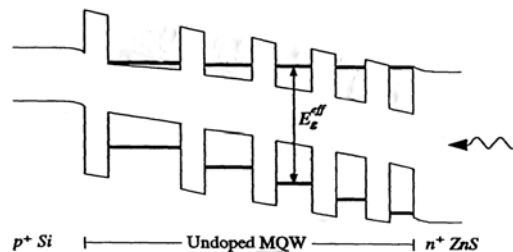


Figure 4. Idealized band diagram of a multiple quantum well (MQW) solar cell. Electronic States in "wells" are "quantized" and therefore have discrete-like energy levels. The mini-band levels depend on the width of the well. K.W.J. Barnham and G. Duggan, *J. Appl. Phys.*, **67**, 7, 1990.

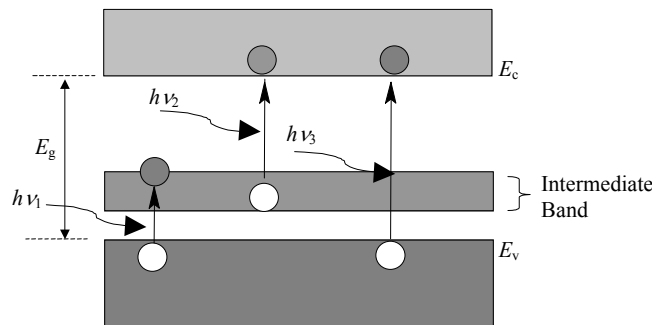


Figure 5. Idealized energy band diagram of an intermediate band quantum dot solar cell (A. Luque and A. Marti, *Phys. Rev Lett.* **78**, 5014 (1997).

Solar Cell Enhancement with Nanostructures

The question which normally arises from a discussion of quantum structures and solar cells is "can these quantum structures truly be used to enhance solar cell performance?" In order to address such a question we must first define what is meant by enhancement. In terms of the theoretical analysis of photovoltaic structures, one normally speaks of either a global or relative efficiency enhancement. For a global enhancement the question that must be answered is "can the efficiency of a nanostructured solar cell under solar illumination be greater than the optimum single-gap cell?" These comparisons normally involve many theoretical idealizations used in calculating limiting efficiencies. In contrast a relative efficiency enhancement refers to

whether in principle and practice a nanostructured solar cell can be more efficient under solar illumination than corresponding single-gap baseline cells for at least some range of baseline cell bandgaps. Finally, there can also be ancillary enhancements, other than just overall devices efficiency, whereby in practice a nanostructured solar cell can offer various advantages over single-gap cells under useful illumination and operating conditions. Several of these advantages that could be especially relevant in terms of space solar power development. For example, it has been demonstrated that a multiple quantum well structured can be more radiation resistant than a non-nanostructured counterpart [9]. Also, these structures can be used to tailor the thermal characteristics of cell to improve cell performance in thermophotovoltaic applications [10].

The question of relative efficiency enhancement was recently addressed when it was demonstrated that GaAs wells in AlGaAs increased efficiency and photocurrent under broadband illumination [11]. However, the observed open circuit voltage drop was inconsistent with original hypothesis and this coupled with larger than optimum E_g of AlGaAs left open the possibility that the wells merely provided bandgap tuning. The case of global efficiency enhancement is even much less clear than that of relative efficiency enhancement and has generated a considerable amount of debate. It was argued that the use of a MQW could be used to extend the spectral response of a solar cell without sacrificing photovoltage [12]. However, shortly thereafter a detailed balance equation calculation was published which showed that the efficiency of a MQW cell was the same as that of an ideal single-gap cell [13]. The assumptions used in this calculation were immediately challenged and a similar calculation with numerical estimates based on real wells actually showed a small global enhancement [14]. However, this result has also been criticized because the absorptivity and emissivity of the structure was treated differently [15]. There have been other models which use more realistic features and may be better suited to real MQW solar cells [16].

The differences in the results of these models could be rectified if it was conclusively known whether or not one should assume uniform quasi-Fermi levels (QFLs) across a MQW solar cell. If not, then the criticisms of the detailed balance analyses would no longer be valid. Several groups have explored the consequences of non-uniform QFLs, most notably in incomplete thermalization [17]. There has been considerable Experimental support for this hypothesis [18].

Detailed balance efficiency limits in QWSCs with non-uniform QFLs, which include two-photon processes, has been calculated to be 63% [19]. (Ironically this is the same exact value that is obtained by Luque and Marti for their intermediate band solar cell (IBSC) utilized quantum dots). In addition, if one allows for reduced carrier transport through hot electron transport, limiting efficiencies could exceed even the 63% mark. Luque, Marti, and Quadra have studied various multiband models thermodynamically and have concluded that if photon-assisted escape is possible then global efficiency improvements are possible [20]. Also, if one neglects hot-electron transport, then the thermodynamic model also predicts 63%. However, Luque, Marti, and Quadra actually argue against non-uniform QFLs citing it would violate the second law of thermodynamics.

It is well accepted that the maximum thermodynamic limit for a single junction conversion of solar irradiance into electrical free energy in the radiative limit using detailed balance is 31% [21]. Therefore, one may view the use of a multi-junction cell approach is actually a means of reducing thermalization losses. (The limit of an infinite number of junctions perfectly matched to a one-sun solar spectrum being 66%). It can thus be argued that quantum structures can exhibit global efficiency improvements by reducing thermal losses. Several approaches to accomplishing this in practice have been outlined [22-24]. However, it must be noted in order to accomplish this the rates of photogeneration of carriers, transport, and interfacial transfer to the contacts must be comparable to the rate of carrier cooling. It has been predicted and experimentally shown that relaxation dynamics can be dramatically altered by quantization (nanostructures, quantum wells, superlattices, quantum wires, and dots). When carriers are confined in potential regions whose dimension is comparable to their deBroglie wavelength or Bohr exciton radius in the semiconductor bulk, their relaxation dynamics are dramatically altered (i.e., hot carrier extraction rates can be comparable to the rate of carrier cooling).

Nanostructured Solar Cell Fabrication

The vast majority of nanostructured photovoltaics have been produced using epitaxial growth involving either molecular beam epitaxy (MBE) or metal organic chemical vapor deposition (MOCVD), which is sometimes referred to as metal organic vapor phase epitaxy (MOVPE). Groups such as the K. Barnham group at Imperial College in London and the A. Zunger group in the Space Vacuum Epitaxy Center or the University of Houston have been leaders in the use of nanostructure growth for photovoltaics. Recently there has been considerable effort in using these similar synthesis techniques to produce photovoltaic structure that incorporates quantum dots as opposed to the quantum wells. These attempts use what is referred to as Stranski-Krastanow growth. This growth technique utilizes lattice strain to produce “islands” of material on a semiconductor surface, and this process can be repeated with alternating complete layers of quantum dots to produce self-organized columnar arrangement of dots (see Figure 6).

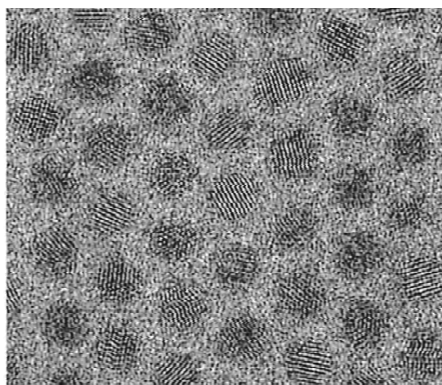


Figure 6. Transmission electron micrograph of self-organized quantum dots (Talpin et. al. *Nanoletters* **2001**, *1*, 207 - 211).

The most widely investigated nanomaterials for polymeric solar cells have been semiconducting nanocrystals, fullerenes, and single wall carbon nanotubes (SWNTs) [28-33]. In particular, CdSe quantum dots (QDs), nanorods, and tetrapods have all shown to improve the performance of solar cells utilizing conjugated polymers. This work has attracted the attention of the space power community for the simple reason that these cells could someday provide specific powers that would be unimaginable for their crystalline counterparts. To date the efficiencies are still in the single digits and the question of stability in a space environment has yet to be addressed.

Conclusions

Ancillary improvements via quantum structures are probably more important to space photovoltaics than any other solar cell application. This is due to the potential they hold for better temperature coefficients, radiation resistance, and spectral shifting. The bandgap tuning available through the use of nanostructures could potentially be integrated into a multi-junction solar cell to add another means to improve current matching. Spectrum shifting through up- and down-conversion could be combined with almost any cell to improve performance. Quantum dots appear to be ideally suited for this application. These nanomaterials and other nanostructures should prove quite useful in new concentrator designs. Nanostructured materials may also hold the key by which polymeric-based cells reach viable efficiencies and become a contender for space solar power applications.

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